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ROTATIONAL RAMAN SCATTERING IN LIQUID OXYGEN

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Plate IV

ABSTRACT. The rotational wing due to liquid oxygen has been studied using a special technique to remove suspended particles from the liquid and a spectrograph capable of resolving the rotational lines of O_2 in the region of 4046 A.U. It has been found that rotational scattering does not consist of sharp lines but it consists of a continuous wing in which the position of maximum intensity is the same as in the case of the gas and also the extent of the wing agrees with that of the rotational Raman spectrum observed in case of gaseous O_2. The significance of the results is discussed.

INTRODUCTION

The distribution of intensity in the continuous spectrum which appears in the neighbourhood of the Rayleigh line in the spectrum of light scattered by many liquids has been studied by various observers.[1] It has been reported by most of these observers that the observed distribution of intensity does not agree with that expected according to the theory of scattering due to free rotation of the molecules. As is well known, if the rotational lines be too close to each other to be resolved by ordinary spectrographs, a continuous rotational wing is expected to appear in the neighbourhood of the Rayleigh line, the intensity in the wing being zero up to a short distance from the centre of the Rayleigh and after rising to a maximum value at a certain distance from the Rayleigh line depending on the moment of inertia of the molecule, falling off gradually and becoming zero at another distance. The observed rotational Raman scattering in the case of liquid hydrogen consists of discrete lines similar to those observed in the case of the gas, but in the case of many other liquids with simple molecules (1) the position of maximum intensity is not clearly separated from the Rayleigh line and (2) the wing extends to a larger distance than expected from the above theory.

Various explanations have been offered to explain this discrepancy. Gross and Vuks[2] attribute the origin of the "wing" in the neighbourhood of the Rayleigh line to lattice oscillations in quasi-crystalline groups of molecules which according to them persist in the liquid state. They observed some new lines in the neighbourhood of the Rayleigh lines in the case of some organic crystals which in the molten state produce intense wing close to the Rayleigh line. They think

that the lines observed in the solid state spread out to form the wing in the liquid state. It has been shown by Sirkar[3] and Sirkar *et al*[4] that the wing cannot have iss origin in the lattice oscillations and there is no quantitative correspondence between the intensity of the new lines observed in the case of any substance in the solid state and that of the wing due to the same substance in the liquid state. Sirkar and Gupta[5] have also pointed out that the observed facts lead to the conclusion that the major portion of the wing is due to rotation of the molecules in the liquid state; but, superposed on it, there is another portion having some other origin.

Bhagavantam[6] put forward the hypothesis that the portion of the wing far away from the Rayleigh line may be due to hindered rotation of the molecules, or, in the other words, to the angular oscillation of the molecules about the position of equilibrium in quasi-crystalline groups Rousset[7] has pointed out that the intensity of the scattered light due to such oscillations varies with the amplitude of oscillation and is negligible for the amplitudes postulated by Bhagavantam

Rousset[8] has put forward different hypotheses to explain the discrepancies mentioned above. According to him the wing extending from the centre of the Rayleigh line consists of two parts, *e.g.*, (1) one part lying within 20 cm^{-1} from the Rayleigh line originating from fluctuation of molecular field, this part being called by him " the Cabannes Daure Effect " and (2) the other part due to rotation of molecules with restricted space quantisation. The restriction in this space quantisation postulated by him is as follows : when the molecule is free to rotate in all directions, the number of molecules in the quantum state J is $(2J+1)e^{-BJ(+1)}$, where $B = \frac{h^2}{8\pi^2 I k T}$ This number is maximum when $(2J+1)^2 = \frac{}{B}$ In the liquid state cybotactic groups are formed and the axis of molecules in such a group can rotate only in one plane and therefore the space quantisation is absent, and the number of molecules in the state J is $e^{-BJ(J+1)}$. This number is maximum when $J = -\frac{1}{2}$ or approximately the position of maximum intensity coincides with the first rotational line. It can be tested by studying the rotational Raman scattering in liquids having simple molecules whether such a restriction in space quantisation actually occurs. In the case of liquid hydrogen, McLennan and McLeod[9] observed two lines with relative intensities the same as observed by Bhagavantam[10] in the case of the gas. But no definite conclusion can be drawn from this fact because the two lines due to the transition $0 \rightarrow 2$ and $1 \rightarrow 3$ are due to para- and ortho-molecules respectively and the relative numbers of these two types of molecules change with time. The next simple diatomic molecule giving intense scattered light is O_2 and the rotational scattering due to gaseous oxygen at various pressures has been investigated thoroughly by Bhagavantam[11] and Trumpy.[12] It has been observed by Trumpy that even at a pressure of 60 atmospheres discrete rotational lines appear in the spectrum of

PLATE IV

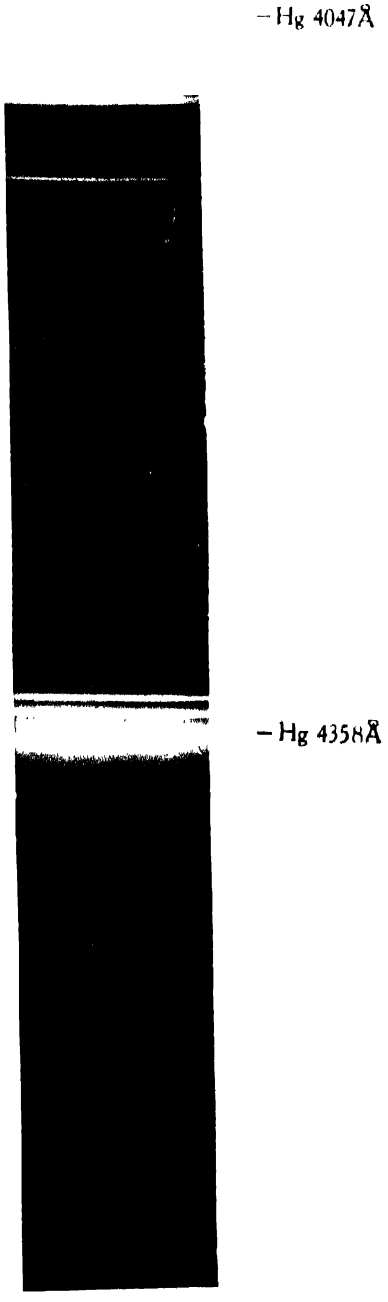

Figure 1

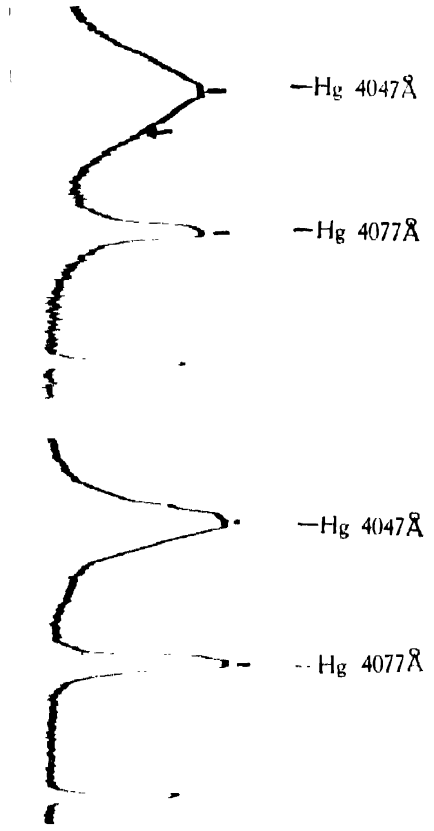

Figure 2 (a) (b)

scattered light and the observed relative intensity of the lines agree with those calculated according to the theory of scattering due to free rotation of the molecules. The lines at 60 atmospheres, however, are much broader than those at 5 atmospheres.

It would be interesting, therefore, to investigate whether similar lines are observed in the case of liquid oxygen. The Raman spectrum of liquid oxygen has, therefore, been studied with suitable technique in order to investigate the distribution of intensity in the rotational wing and the results are discussed in the present paper.

EXPERIMENTAL

The main difficulty in recording the rotational wing due to liquid oxygen is due to the fact that the commercial liquid oxygen when exposed to atmosphere becomes turbid owing to the condensation of moisture and the formation of small particles of ice in the liquid. These ice particles scatter light very strongly and hence the Rayleigh line becomes over-exposed and spread out so as to mask the rotational wing. In the present investigation an arrangement was made to prevent the formation of ice particles in the liquid oxygen used. The liquid oxygen supplied by the local manufacturers was contained in a vertical unsilvered Dewar vessel of Pyrex glass ; but, before introduction into the vessel, the liquid underwent three stages of filtration, the first stage being through a bed of solid carbon dioxide and the other two through filter papers only. The first filter bed was present at the mouth of the Dewar vessel throughout the exposure and thus prevented subsequent absorption of moisture by the liquid air below. The liquid was illuminated by light from two mercury arcs focussed by two large glass condensers of short focal length. Also a metallic curved reflector at the back of each lamp was used to improve the illumination. A Fuess glass spectrograph with a dispersion of about 11·5 A.U. in the region 4046 A.U. was used. The Stokes side of the Hg-line 4046 A.U. obtained with this spectrograph is free from coma for moderate intensities but when the exposure is long enough to record the 4145 A.U. line of Hg, the line 4046 A.U. spreads up to about 30 cm^{-1} from the centre of the line. The spectrograph can, however, resolve clearly about 11 cm^{-1} in this region, and, as the distance between two successive rotational lines of O_2 is 11·5 cm^{-1}, this spectrograph can resolve these rotational lines excited by 4046 A. U and is almost as efficient as that used by Trumpy in his investigation on the rotational Raman spectrum of O_2. Both Ilford Special Rapid and Golden Iso-zenith plates were used and two good spectrograms, one on each of the above plates were obtained. In each case a continuous exposure of 15 hours was given and liquid oxygen was added every half an hour. The room was darkened sufficiently to prevent any stray daylight from entering into the spectrograph by scattering and reflection. The spectrum of Hg-light was also photo

graphed in such a way that its density of the lines was almost the same as that in the spectrogram due to the scattered light obtained on the same plate.

RESULTS AND DISCUSSIONS

The spectrogram of the scattered light as well as the microphotometric records of the scattered and incident Hg-line 4046 A. U. obtained with a Moll's self-registering microphotometer are produced in plate IV. It can be easily observed that no discrete rotational lines have appeared, but only a continuous wing has been obtained. The wing extends up to about 140 cm^{-1} from the Rayleigh line on the Stokes side and this agrees with the extent of the rotational Raman spectrum due to the gas recorded by Trumpy. Also the position of the maximum intensity in the wing is at a distance of about 50 cm^{-1} from the centre of the Rayleigh line and agrees with that of the most intense rotational lines observed by Trumpy. Of course, in the microphotometric record this maximum intensity is not represented by any pronounced peak owing to the presence of a coma close to the Rayleigh line but a narrow gap has been observed in the spectrogram between the edge of the coma and the intense portion of the wing. This gap is visible with an ordinary magnifying lens but the microphotometric record taken even with a fine thermopile slit shows only an inflection (indicated in fig. 2(*a*) plate IV by the arrow).

The above result leads to the conclusion that in the case of the simple diatomic molecule like O_2 in the liquid state the rotational lines become much broader than those in the case of molecules in the gaseous state, even at a pressure of about 60 atmospheres. This is probably due to the effect of intermolecular field in the liquid state. At higher pressures in the gaseous state this intermolecular field begins to show its influence on the width of the line. The widening at 60 atmospheres is not very large and it can be correlated to the fact that the intermolecular field at the pressure in the gaseous state compared to that in the liquid state is small. The intermolecular field in the gaseous state may be identified with the van der Waals' force, $\frac{a}{V^2}$ and that in the liquid state may be indentified with the internal pressure $\left(\frac{\partial u}{\partial V}\right)_T$, *i.e.*, the force per sq. cm. with which the molecules are drawn inwards. Tentatively we may compare the van der Waals' force, $\frac{a}{V^2}$ for gaseous oxygen at 60 atmospheres and the internal presssure $\left(\frac{\partial u}{\partial V}\right)_T$ of liquid oxygen at its boiling point. Unfortunately the data in the desired region of temperature and pressure are not available. However it may be useful to calculate $\frac{a}{V^2}$ and $\left(\frac{\partial u}{\partial V}\right)_T$ near about the desired region.

It can be shown that $\frac{a}{V^2} = (\alpha_p T_0 - 1) p_0$ where α_p is the mean pressure coefficient between 0° and 100°C, and p_0 = pressure in atmosphere and $T_0 = 273{\cdot}2$. The value of α_p for gaseous oxygen at 100 atmosphere is available. The value of α_p at 60 atmospheres will, however, be much smaller. Using this larger value for $\alpha_p = {\cdot}00492$, the van der Waals' force, $\frac{a}{V^2}$ becomes about 20 atmospheres. The correct value is certainly much less, because α_p is much less at 60 atmospheres.

It can be shown from thermodynamical considerations that the internal pressure $\left(\frac{\partial u}{\partial V}\right) = T E \alpha_v - p$,

where E = modulus of bulk elasticity,

and α_v = coefficient of volume expansion.

In the case of liquid O_2 the values of α_v and compressibility $\beta \left(= \frac{1}{E}\right)$ at 20·2°K are available. Assuming these values of α_v and β to be valid at the boiling point of the liquid oxygen, $\left(\frac{\partial u}{\partial V}\right)$ is about 60 atmospheres. This value of internal pressure is quite large as compared with the value of $\frac{a}{V^2}$ for gaseous O_2 at 60 atmospheres. Although this value of internal pressure is quite small in comparison with that calculated in case of other substances in the liquid state, it is many times larger than the value of $\frac{a}{V^2}$, calculated at 60 atmospheres. Hence it seems that the observed broadening of the rotational lines in case of liquid state may be correlated with the internal pressure.

The space quantisation, however, is not restricted in this case by the formation of cybotactic groups in the liquid, because in that case the position of maximum intensity would coincide with the first rational line and would be at a distance of 14·4 cm^{-1} from the centre of the Rayleigh line. As already mentioned, the observed distance of the position of maximum intensity is at about 50 cm^{-1} from the centre of the Rayleigh line.

The vibrational Raman line of O_2 at $\Delta\nu$ equal to 1550 has been recorded with large density and no other faint vibrational Raman line has been observed in the spectogram. This fact shows that percentage of any complex molecule such as O_4, if such molecules are present in the liquid, is very small. Hence this rotational wing is not affected by the presence, if any, of such molecules in the liquid. The scattering due to fluctuation of intermolecular field is not very intense in this case, because, as can be seen from the comparison of the microphotometric records of the scattered and the incident lines, the top portion of the

curve due to scattered line is not much broader than that due to incident line, but the curves show the presence of feeble Cabannes Daure effect. The principal effect of the intermolecular field is therefore to make each individual rotational line broader. In the case of molecules with larger moment of inertia, the position of maximum intensity is much nearer to the centre of the Rayleigh line, *e.g.*, in case of benzene the position of maximum is at 26 cm^{-1} from the centre of the Rayleigh line. If the individual lines become much broader in the liquid state, the maximum becomes flattened. It is evident, therefore,that if the Cabannes Daure Effect is superimposed on the rotational wing in the case of the liquid state, the probability of observing a position of pronounced maximum intensity in the wing diminishes very much.

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REFERENCES

1 Weiler, *Z. f. Phys.*, **68**, 782 (1930) ; Ranganatham, *Ind. J. Phys.* **7**, 353 (1932); Bhagavantam, *Ind. J. Phys.*, **3**, 197 (1933) ; Bhagavantam and Rao, *Ind. J. Phys.*, **8**, 437 (1934); Rao, *et al*, *Proc. Ind. Acad. Sc* , **1**, 273 (1934).

2 Gross, and Vuks, *Nature*, **135**, 100, **431**, 998 (1935)

3 Sirkar, *Ind. J. Phys.*, **10**, 75 (1936).

4 Sirkar and Mookerjee, *Ind. J. Phys.*, **10**, 375 (1936); Sirkar and Gupta, *Ind. J. Phys.*, **12**, 35 (1938).

5 Sirkar and Gupta, *loc. cit*

6 Bhagavantam, *Proc. Ind. Acad. Sc.*, **2**, 63 (1935).

7 Rousset, *Jour. de Phys.*, **6**, 507 (1935).

8 Rousset, *loc. cit.*

9 McLennan and McLeod, *Nature*, **123**, 116 (1929).

10 Bhagavantam, *Ind. J. Phys.* **7**, 107 (1932)

11 Bhagavantam, *Ind. J. Phys.*, **6**, 319 (1931).

12 Trumpy, *Z. f. Phys.* **84**, 282 (1933).